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RESIPROCATING ENGINE APPLICATIONS

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Thin Film Mixed Potential NO_x Sensor Development for Stationary Reciprocating Engine Applications

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ABSTRACT

Mixed potential sensors using thin film Mg-doped LaCrO₃ working electrodes, Pt counter electrodes, and thin film YSZ electrolytes on Al₂O₃ polycrystalline substrates were prepared and studied at 600 and 650°C in 10.4% O₂/N₂ balance and in air atmospheres for NO, NO₂, CO, and hydrocarbon responses. The lanthanum chromite-based sensors showed preferential sensitivity to NO₂ with cross sensitivity to CO and non-methane hydrocarbons such as C₃H₆ and C₃H₈. In contrast, sensors with spinel NiCr₂O₄ working electrodes show minimal sensitivity to NO₂. The use of a heated Pt black pre-catalyst upstream to the sensor was demonstrated and the use of this pre-catalyst effectively removed the CO and hydrocarbon response however more work needs to be done to understand the NO/NO₂ chemistry post catalyst. Studies conducted for up to 800 hrs at 600°C show minimal aging in these devices.

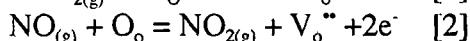
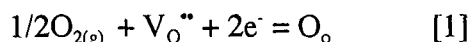
INTRODUCTION

Reciprocating, internal combustion gas engines are the fastest-selling and least expensive distributed energy generating systems in the world today (1). Commercial reciprocating engine systems using natural gas are available to produce power from 0.5 kW to 10 MW and have efficiencies between 37 and 40 percent. NO_x emissions can be as low as 1 gram/hp-hr. Reciprocating gas engines are well suited for small-scale power generation and provide high reliability, inexpensive back-up power, power for remote locations, and power production during peak times to reduce business costs. Some of the principal goals of the DOE's Advanced Reciprocating Engine System (ARES) program are to improve fuel efficiency and flexibility, and reduce emissions of reciprocating engine systems used for distributed energy generation applications.

Advanced reciprocating engines require new sensor technologies to reduce emissions and to improve overall combustion efficiency. Engine feedback control, NO_x emissions monitoring and control, and sensors to control the regeneration of reduction catalysts are required. The NO_x emissions target for natural gas-fired reciprocating engines is 0.1 g/bhp-hr (roughly a factor of ten reduction from current levels). A new NO_x sensing technology is necessary to meet the sensor requirements for low cost, sulfur tolerance, and a long, stable lifetime. The sensors developed over the last decade for lean-burn

gasoline engines cannot meet all of these requirements. In our past work, we have developed CO and HC mixed potential sensors based on doped zirconia (2-4) and ceria (5) electrolytes and metal oxide electrodes for automotive on-board diagnostic applications.

Mixed potential sensors based on oxygen ion conducting electrolytes have been investigated extensively for the detection of CO, H₂, HCs, and NO_x. The competing reactions of oxygen reduction (oxidation) and NO oxidation and NO₂ reduction establish the mixed potential at an electrode. Equations 1-2 illustrate this for NO/NO₂.



In these equations, V_O^{••} is an oxygen vacancy and O_o is a lattice oxygen in the electrolyte. Depending on the rates of the two reactions, a non-equilibrium potential that is more negative (positive for NO₂ reduction) than that predicted by the Nernst equation develops under oxygen rich conditions (6). This mixed potential, being dependent on kinetic factors, is expected to be a strong function of the electrode material (7).

The first reported mixed potential sensor utilized an yttria-stabilized zirconia electrolyte with gold and platinum metal electrodes (8). Since then, many other groups have investigated mixed potential sensors based on oxygen ion-conducting solid electrolytes for the detection of CO, H₂, HCs, and NO_x (2-19). We have explored the use of mixed potential sensors based on dual metal oxide electrodes for automotive applications (2-4). We continue this work with emphasis on selecting refractory metal oxide electrode/electrolyte materials and sensor designs that will withstand the rigors of the reciprocating engine exhaust environment.

EXPERIMENTAL

Mg doped LaCrO₃ thin films were prepared using RF magnetron sputtering via fluoride/metal composite (off-axis) targets. A stoichiometric amount of LaF₃, SrF₂ and chromium metal (average particle size < 10 μm) - to yield a cation ratio of La:Mg:Cr = 0.8:0.2:1 and La:Mg:Cr = 1:0.2:0.8 - were weighed and placed into a polypropylene ball mill container along with isopropyl alcohol and zirconia grinding media. The mixture was ball-milled for 6 hours. The slurry was collected and dried at 50°C. The powder was then placed into a 2" diameter steel die and pressed at 400 pounds total pressure for 5 min. The completed powder sputter target was transferred to a RF magnetron sputter system.

A 1 cm² Al₂O₃ substrate was masked such that a 4.3mm x 10 mm stripe of the substrate was exposed to the sputter target. Prior to mounting, the substrates were ultrasonically cleaned in isopropanol or acetone and then dried and fired in air at 1100°C for several hours. The Al₂O₃ wafers were mounted onto a Ni faceplate that was subsequently placed into contact of a boron nitride heater specifically designed for vacuum operation. The substrate was typically held to the Ni faceplate by an alumina mask held by a metal clip or the substrate could be glued to the faceplate using a water-

based, silver epoxy (AREMCO). The substrate temperature was monitored using a type K thermocouple embedded within the Ni faceplate. To measure thickness and deposition rates, a masked piece of polished sapphire was mounted next to the substrate. The step created on this witness sample from the shadow mask was then used to measure the film thickness produced in the PVD run using a DEKTAK profilometer. The sputter deposition was carried out at 400°C. The films were grown in a UHP Ar atmosphere at 40 mTorr pressure and at a power setting of 125W.

After sputtering, the fluoride/chromium films were removed from the deposition system, placed into an alumina boat, and transferred to a tube furnace. A switching system was set-up to switch from dry Ar to humidified Ar (gas bubbled through water at 25°C) using a three-way valve. The films were heated at 10°C/min to 800°C in dry Ar. At 800°C the gas was switched to humidified Ar and the sample was annealed at 800°C for 15 minutes. The thin film sample was heated to 1000°C in dry Ar and held for an hour to allow for grain growth in the film.

Following deposition and subsequent post reaction/annealing (if required), the films were characterized using a variety of techniques. A Siemens D5000 x-ray diffractometer (XRD) using $\text{CuK}_{\alpha 1}$ radiation was used to determine the film crystal structure, phase purity and lattice parameters. A complete description of this procedure can be found in (20).

A 5000Å thick Pt counter electrode was sputtered onto the substrate, parallel and coplanar to the metal oxide electrode. At this time a small, 3 mm x 3 mm Pt pad approximately 5000Å thick was sputtered on a section of the metal oxide electrode to facilitate the attachment of a Pt lead wire to make electrical contact with the metal oxide, sensing electrode. The substrate was finally transferred to an electron beam evaporation chamber to cover the electrodes with a 5 to 10 μm thick, thin film of 8 mole% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ electrolyte. The source material for this film was crushed CeraFlex™ brand YSZ obtained from MarketTech International. As before, a masked sapphire witness and profilometry was used to determine grown rate and film thickness and XRD was used to insure phase purity.

0.04" thick Pt lead wires were attached to the Pt pad and Pt counter electrode using a parallel gap wire bonded. The completed sensor was transferred to a tube furnace for testing. A computer-controlled Keithley 2400 source meter was used to measure voltage levels at open circuit.

RESULTS AND DISCUSSION

The first sensor studied used a metal oxide working electrode that was B-site doped with Mg or $\text{LaCr}_{0.8}\text{Mg}_{0.2}\text{O}_3$. The thickness of this electrode was measured to be roughly 5000Å. Figure 1 is the initial sensor response to NO_2 after the sensor was heated to 650°C in an atmosphere of 10.4% O_2/N_2 balance flowing at 500 sccm. The base gas was premixed and analyzed using a commercial Rosemount O_2 analyzer. The sensor showed excellent reproducibility in voltage level as the NO_2 concentration was cycled from 0 to

100 ppm. Response time to 90% of level at 650°C was approximately 10 seconds. The methane cross sensitivity is an important consideration for the ARES project goals. Figure 2 is the plot of both NO₂ and CH₄ sensitivity for 650°C and shows almost no sensitivity towards methane. The NO₂ sensitivity versus PO₂ dependence was also measured at 1, 10.4, and air: the voltage level for 100 ppm of NO₂ changed approximately 2.4 mV/% change in oxygen partial pressure. After testing and annealing at 650°C – this annealing time served to “burn-in” the device prior to lifetime testing – the temperature of the sensor was lowered to 600°C.

The sensor response to fixed concentrations of NO, C₃H₆, C₃H₈, CO, and CH₄ were studied. Figure 3 is the sensor response to these gases at 600°C in addition to NO₂. Lowering the temperature 50°C decreased (increased in magnitude) the NO₂ voltage from -34 mV to -40 mV. The response time for NO₂ to 90% of level increased to 12 seconds. With these test conditions, the sensor showed preferential sensitivity to NO₂ (0.40 mV/ppm NO₂ as compared to 0.071 mV/ppm C₃H₆ and 0.0053 mV/ppm CH₄).

After another period of soaking, the voltage level for NO₂ was monitored with time for 800 hrs annealing at 600°C. The voltage levels for 100 ppm NO_x and 500 ppm CO/HC were measured periodically. Figure 4 is a plot of only the sensor output for 100 ppm NO₂. The slope of this line is indicated in the figure and, for NO₂, the sensor voltage increased (more negative voltage and became more sensitive to NO₂) at a rate of 0.17mV/day over this period of testing. The change in levels for NO, CO, and the HCs were varied and ranged from a decrease in sensor voltage (i.e. became less sensitive) -0.0017mV/day for C₃H₈ to -0.043 mV/day for C₃H₆.

To explore and demonstrate possible approaches to control and increase sensitivity to NO₂ (or conversely to enhance sensitivity of the sensor to NO) and decrease cross sensitivity toward CO and HCs, we briefly looked at other possible metal oxide materials and examined whether precatalytic treatment (i.e. a small catalyst placed upstream to the sensor) of the test gas was possible. Figure 4 shows the effect of the placement of a Pt black catalyst at 200 and 400°C versus no catalytic pretreatment of the test gas. Figure 4 demonstrates that by 400°C, the Pt black eliminates CO and the hydrocarbons. However, there is a clear effect on the NO_x chemistry as can be inferred from the NO and NO₂ voltage levels. The Pt catalyst at 400°C oxidizes the NO to NO₂ however the voltage level is roughly half of the voltage level measured without the catalyst present. Most likely a sufficient quantity of NO is being produced via NO₂ reduction to reduce the voltage measured by the sensor. More study will be necessary with the assistance of an independent NO_x analyzer.

Two additional metal oxide electrodes were also studied in this work. One sensor was fabricated with three electrodes: one A-site doped LaCrO₃ (La_{0.8}Mg_{0.2}CrO₃), one B-site LaCrO₃ (LaMg_{0.2}Cr_{0.8}O₃), versus a Pt counter and a spinel/Pt device with a NiCr₂O₄ electrode. Figure 6 is plot of the voltage output of the 3-terminal device (the voltages are each measured against the Pt counter electrode) in air at 550°C after 900 hrs of annealing at this temperature for 100 ppm of NO₂ and NO, and 500 ppm quantities of C₃H₆, C₃H₈, CO, and CH₄. Both electrodes show trends in sensitivity already observed with the

previous device. Both A-site and B-site electrodes show similar sensitivity to the various test gases. In contrast, Figure 7 shows that a NiCr_2O_4 working electrode shows preferential sensitivity towards non-methane hydrocarbons under similar testing conditions. This suggests the exciting possibility of fabricating mixed potential sensors using combinations of metal oxide electrodes to enhance NO_x sensitivity. More work is obviously needed.

CONCLUSIONS

This work demonstrates a device with preferential sensitivity towards NO_2 with minimal sensitivity to CH_4 , in addition to sufficient lifetime, stability, and response reproducibility in line with the goals of the DOE's ARES program. The cause in the change in sensor EMF with time – even after a substantial break-in anneal at 650°C – is not understood and needs to be studied more. However, the rates of aging shown in this work are substantially less than typically found in mixed potential sensors that use Au working electrodes. While preferential sensitivity towards NO_2 was demonstrated with the devices in this work, reduced sensitivity towards HC's and CO would be highly desirable and needs to be studied in future work. Moreover, the ability to tailor a device to preferentially sense NO with respect to NO_2 would also be highly desirable specifically given the intended application in the ARES project. Other metal oxide electrodes will be studied in the near future. The use of catalysts to pre-treat the test gas mixture and the effects on gas phase chemistry will also be explored in the near future.

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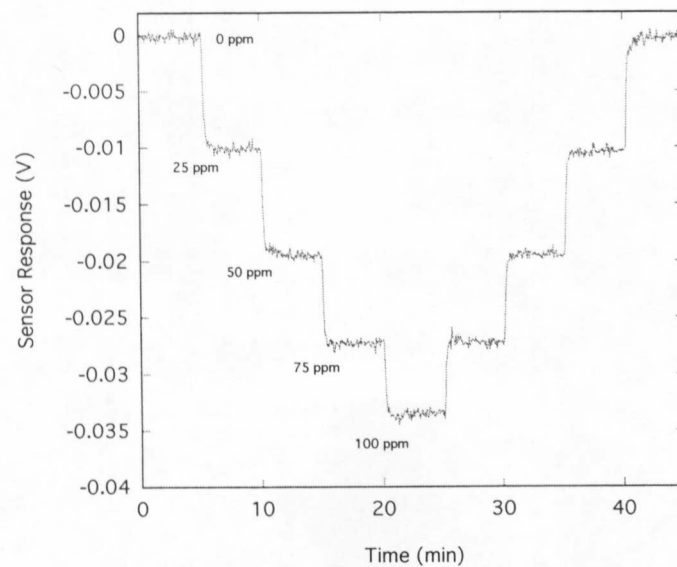


Figure 1. Initial NO₂ response, 0-100 ppm, at 650°C, 10.4 % O₂/N₂ balance flowing at a base flow rate of 500 SCCM.

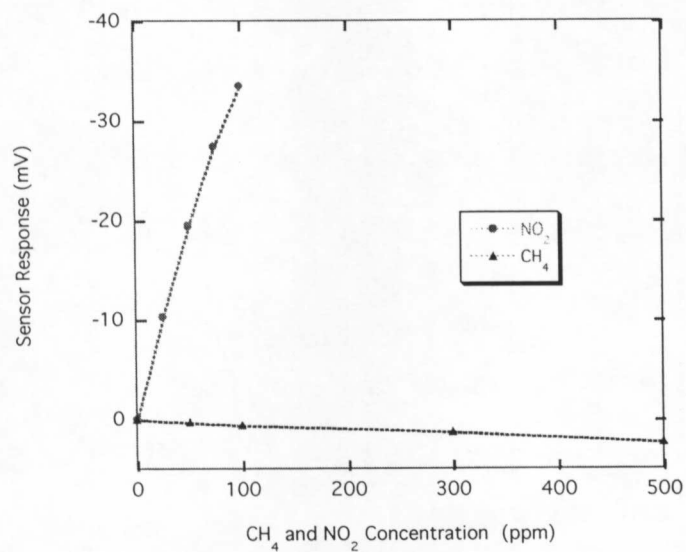


Figure 2. Sensor response to NO₂ and CH₄ at 650°C and in 10.4% O₂.

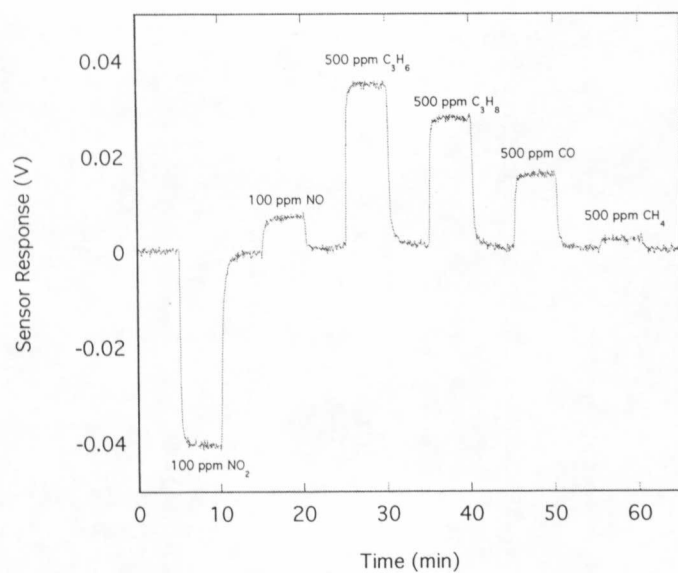


Figure 3. Cross sensitivity studies: sensor response to NO_2 , NO, and selected HC's and CO versus time at 600°C . Base gas is 10.4% O_2 at a flow rate of 500 SCCM.

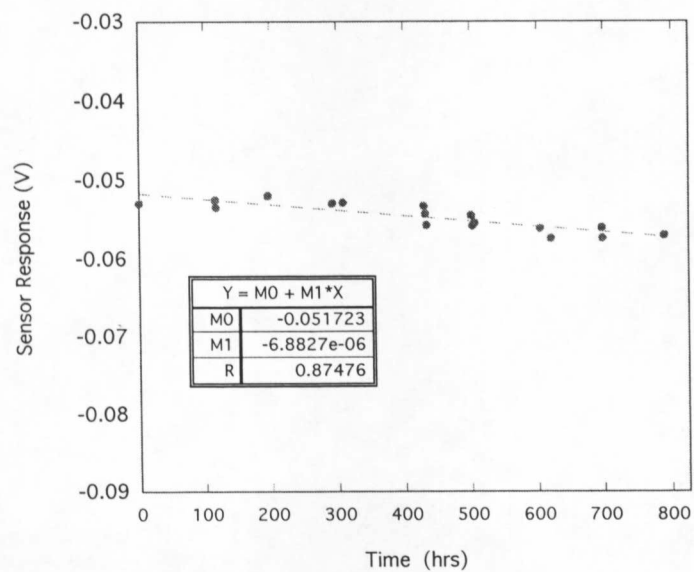


Figure 4. Plot of sensor voltage measured at 100 ppm of NO_2 versus a time period of 800 hours at 600°C in 10.4% O_2 .

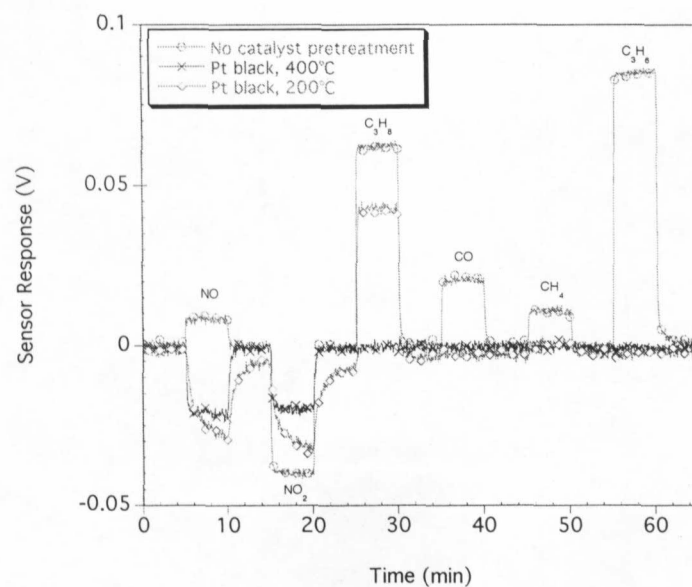


Figure 5. Mixed potential response of a sensor with an A-site metal oxide electrode versus Pt counter electrode at 550°C for 100ppm NO, NO₂, and 500 ppm of C₃H₈, CO, CH₄, and C₃H₆. Base gas flow is air at 500 SCCM flowing through a pre-treatment catalyst of a commercial catalyst consisting of unsupported Pt black.

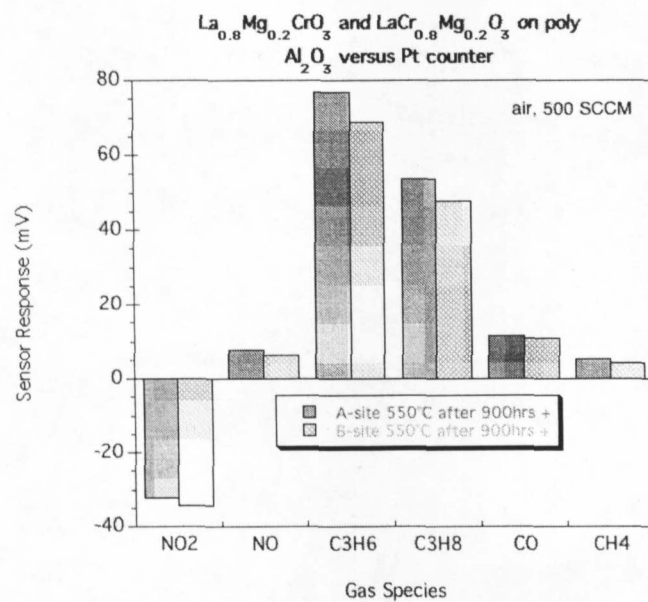


Figure 6. A comparison of A-site and B-site Mg-doped LaCrO₃ thin film working electrodes versus a Pt counter electrode in 500 sccm of air at 550°C. Gas concentrations are 100 ppm of NO₂ and NO and 500 ppm of C₃H₆, C₃H₈, CO, and CH₄.

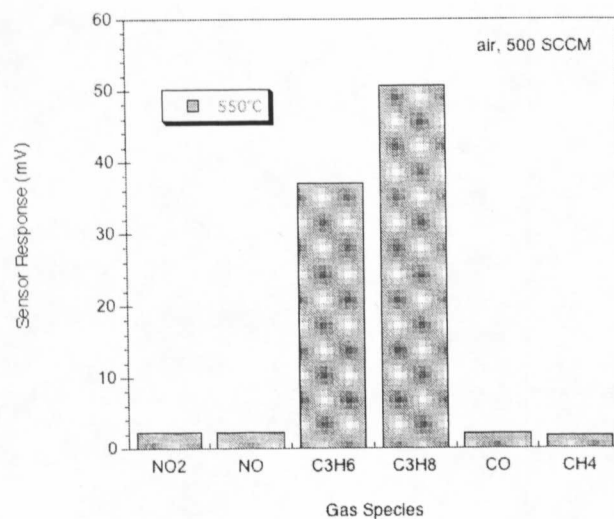


Figure 7. Two electrode sensor response to 100 ppm of NO₂ and NO and 500 ppm of C₃H₆, C₃H₈, CO, and CH₄ in air at 550°C. Voltages are measured against a Pt counter electrode.